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## Photophysics of solar fuel materials

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# Summary

The energy of sunlight can be used to drive a chemical reaction that is thermodynamically uphill. High energy molecules that are produced in this way are called 'solar fuel'. To improve the solar-to-fuel energy conversion efficiency, it is important to understand the photophysical pathways that lead to—or compete with—fuel production. In this thesis transient absorption spectroscopy (pump-probe) is used to study the photophysics of various materials in the context of solar fuel research.

Chapter 1 is an introductory chapter on solar fuel research and transient absorption spectroscopy. Chapter 2 presents the study of a carotenoporphyrin and a carotenofullerene dyad. Upon excitation of the carotenoid in these dyads, electron transfer, excitation energy transfer and charge recombination processes occur. Surprisingly, the excitation energy transfer process is absent in the carotenoporphyrin dyad.

The caroteno-phthalocyanine dyad in Chapter 3 gives rise to a complex transient absorption signal, which is explained by the presence of three subpopulations in the sample. The subpopulations are proposed to originate from rotation of the carotenoid with respect to the phthalocyanine. The first subpopulation shows the spectral features of excitonic coupling: a spectrum with both carotenoid and phthalocyanine signatures is present directly after excitation. The second subpopulation shows the characteristics of excitation energy transfer from phthalocyanine to carotenoid and the third that of independent phthalocyanine decay.

Chapter 4 presents the photophysics of a phenol–pyrrolidino[60]fullerene dyad. Upon excitation of the fullerene a proton-coupled electron transfer (PCET) process is found. Exchange of the proton with deuterium leads to a threefold reduction of the PCET rate. This kinetic isotope effect shows that the proton and electron are transferred in a concerted manner.

In Chapter 5 the spectroscopic analysis of a molecular triad is reported. A porphyrin electron donor is covalently linked to both a cyanoporphyrin acceptor and a benzimidazole-phenol model for the Tyr<sub>z</sub>-D<sub>1</sub>His190 pair of PSII. Photoinduced electron transfer from the porphyrin to the cyanoporphyrin was

observed, but in contrast to a previous study of a related molecule, the formation of a long-lived charge separated state was not detected.

Chapter 6 is a study of the semiconductor bismuth vanadate,  $\text{BiVO}_4$ . This study elucidates the dynamics of electrons and holes that follows excitation of the semiconductor. The photophysics includes trapping of electrons and holes and recombination with a trap-limited rate.

Chapter 7 describes the implementation of a second laser in the existing femtosecond to nanosecond transient absorption spectroscopy setup. In the resulting dual-laser setup the range of timescales is extended to the millisecond timescale, while maintaining the femtosecond resolution.